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ON THE RAMAN SPECTRA AND HEAT CAPACITY OF BENZENE AT LOW TEMPERATURES

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(*Received for publication, March 31, 1930*)

Plate VI

ABSTRACT The Raman spectra of solid benzene at $-10°C$, $-100°C$ and $-180°C$ have been investigated. At $-183°C$ five new lines have been observed in the low frequency region at 47, 53, 78, 95 and 131 cm^{-1} respectively. It is observed that the lines 44, 60 and 100 cm^{-1} appearing at $-10°C$ become more intense and shift to 53, 78 and 134 cm^{-1} respectively at $-180°C$ and two more new lines appear at the latter temperature. The values of C_v calculated on the assumption that three frequencies, 58, 99 and 135 cm^{-1} contribute to the Einstein function at low temperatures between 4°K and 70°K are found to agree fairly well with the observed values. It is pointed out that if the line 35 cm^{-1} observed at about 0°C is taken to be that due to complete rotation of the molecule about an axis perpendicular to its plane, as has been done by Rousset (1944), the calculated values of C_v become many times higher than values observed for temperatures between 4°K and 20°K. It is concluded that at low temperatures virtual bonds are formed between adjacent molecules and oscillations in these groups produce the new Raman lines in the low frequency region.

INTRODUCTION

The Raman spectrum of benzene in the solid state was first studied by Gross and Vuks (1935) who discovered two new lines at 63 cm^{-1} and 108 cm^{-1} respectively. It was later reported by one of the authors (Sirkar, 1936) that at a temperature of $-180°C$ benzene in the solid state yielded three new lines having frequency shifts 81 cm^{-1}, 98 cm^{-1} and 124 cm^{-1} respectively, instead of the two lines mentioned above. Sirkar and Gupta (1938) also calculated the specific heat of solid benzene at low temperatures along with that for a few other compounds and showed that the values of C_p calculated by taking into account Einstein functions corresponding to the new lines in the low-frequency region, besides the Debye function, agree with the observed values. Kastler and Fruhling (1944) recently studied the Raman spectrum of a single crystal of benzene at a temperature just below its freezing point and also studied the polarisation of the new lines in the low frequency region. They observed four new lines at 35 cm^{-1} cm^{-1} and 100 cm^{-1} and found that the line 35 cm^{-1} is totally polarised. They concluded from these results that the lines 55 cm^{-1}, 65 cm^{-1} were due to rotational oscillations of the benzene molecule, pivoted in the crystal lattice, about the *b*-axis and the line 100 cm^{-1} was probably due to similar oscillation of the molecule about an axis perpendicular to *b*-axis. Rousset

(1944) next calculated the specific heat of solid benzene at low temperatures taking into account the Einstein functions corresponding to these lines and taking the line 35 cm^{-1} to be due to complete rotation of the molecule about an axis perpendicular to its plane. He, however, overlooked the fact reported by Sirkar (1936) that the frequency-shifts of the new lines in the low frequency region observed in the case of solid benzene increase with the lowering of temperature.

As regards the hypothesis put forward to explain the origin of these lines by Kastler and Rousset (1941) and also independently by Bhagvantam (1941) it has been pointed out earlier by one of the authors (Ray, 1950) that it can be tested only by studying the changes which the new lines undergo in intensity and position with the lowering of temperature of the crystal. Further, in any attempt to calculate the specific heat of the crystal at very low temperatures the accurate values of the frequencies of the new lines at these temperatures should be used. It has already pointed out that in the line at 35 cm^{-1} was not observed by Sirkar (1936) in the case of benzene in the solid state at $-180°C$ and this may be due to photographic spreading of the over-exposed Rayleigh line, as indicated by the microphotometric records reproduced by him. Thus accurate data regarding the frequency-shifts of all these new lines which may be observed in the case of solid benzene at very low temperatures were not known. It was, therefore, thought worthwhile to reinvestigate the Raman spectra of solid benzene at different temperatures going down up to about $-180°C$, using an improved technique, and to discuss the bearing of the results on the theories which have been put forward by previous workers to explain the origin of the new lines and also on the specific heat of solid benzene at low temperatures.

EXPERIMENTAL

Benzene used in the present investigation was obtained from U. S. A. and was of pure quality. It was distilled in vacuum before use. The arrangement used for studying the Raman spectra of solid benzene at different temperatures is the same as that described by Majumdar, (1949) Care was taken to solidify the liquid slowly in order to obtain a homogeneous mass so that the proportion of stray light due to diffuse reflection from the volume of the crystal was very small. The Fuess spectrograph used in the present investigation is more suitable than that used by one of the authors earlier (Sirkar, 1936), because it has a dispersion of about 10.8 Å/mm and the line 4046 Å is free from coma on the Stokes side, while in the case of the spectrograph used earlier the dispersion was slightly smaller. The Raman spectrum of solid benzene was photographed at three different temperatures, e. g., $-10°C$, $-100°C$ and $-180°C$. These temperatures were produced in the region in which the sealed Pyrex tube containing the liquid was placed inside a transparent Dewar vessel by adjusting the level

of the liquid oxygen in this vessel. Iron arc spectrum was photographed in each spectrogram as comparison.

RESULTS AND DISCUSSION

The spectrograms are reproduced in Plate VI along with that for liquid benzene for comparison. As only the prominent lines appeared in the spectrograms due to solid benzene, no attempt was made to record the faint lines due to the liquid. The frequency-shifts of the prominent lines are given in Table I.

TABLE I

Benzene

Liquid at 30°C $\Delta\nu$ in cm^{-1}	Solid at −10°C $\Delta\nu$ in cm^{-1}	Solid at −100°C $\Delta\nu$ in cm^{-1}	Solid at −180°C $\Delta\nu$ in cm^{-1}
Continuous wing			47 (1) · *e*, *k*.
extending up to	44 (1), *e*, *k*	48 (2) *e*, *k*	53 (2) *e*, *k*
150 cm^{-1}	60 (1b), *e*, *k*	69 (6) *e*, *k*	78 (5) · *e*, *k*
			95 (1b) : *e*, *k*.
	100 (1b), *e*, *k*	116 (*b*) *e*, *k*	134 (3) : *e*, *k*
607 (3), *e*, *k*	603 (1), *e*, *k*	603 (1) *e*, *k*	603 (1) : *e*, *k*
849 (2*d*), *e*, *k*.	850 (2) ; *e*, *k*	852 (2) *e*, *k*	855 (2) . *e*, *k*
992 (10), *e*, *i*, *k*	990 (10), *e*, *i*, *k*	990 (5) *e*, *i*, *k*	989 (10) *e*, *i*, *k*.
1178 (3*d*), *e*, *k*	1174 (3), *e*, *k*	1174 (4). *e*, *k*	1174 (4) · *e*, *k*.
1586 (3), *e*, *k*	1583 (3), *e*, *k*	1582 (2) *e*, *k*	1581 (3) · *e*, *k*
1608 (2), *e*, *k*	1604 (2), *e*, *k*	1603 (1) *e*, *k*.	1602 (2) *e*, *k*.
3049 (3), *e*, *i*, *k*	3049 (3) ; *e*, *i*, *k*	3042 (2) · *e*, *i*, *k*.	3042 (2) · *e*, *i*, *k*
		3046 (2). *e*, *i*, *k*	3046 (2) . *e*, *i*, *k*
3065 (5), *e*, *i*, *k*	3063 (5) ; *e* *i*, *k*	3063 (5). *e*, *i*, *k*	3063 (5) *e*, *i*, *k*.

It can be seen from Table I that the remarkable change which takes place in the Raman spectrum of benzene with the solidification of the liquid is the appearance of the new lines in the low frequency region. At a temperature of about −10°C the crystal yields three new lines at 44, 60 and 100 cm^{-1} respectively. This fact seems to be in agreement with that observed by Kastler and Fruhling (1944) ; if it is assumed that the line at 60 cm^{-1} consists of a close doublet, and the line at 35 cm^{-1} observed by them, presumably at about 0°C, shifts to about 44 cm^{-1} at −10°C. When the crystal is cooled down to −100°C the three lines shift respectively to 48, 69 and 116 cm^{-1}. On further cooling the crystal up to −180°C, the lines

at 48, 68, and 116 cm^{-1} shift to 53, 78 and 134 cm^{-1} respectively and two more faint lines appear at 47 cm^{-1} and 95 cm^{-1} respectively. The intensity of the lines 48, 68 and 116 cm^{-1} relative to that of the line 990 cm^{-1} increases considerably and these lines become sharper, with the lowering of the temperature

As regards the prominent Raman lines due to intramolecular oscillations of the benzene molecule, it is observed from Plate VI that all the lines become extremely sharp as the liquid is solidified and the line 3049 cm^{-1} due to C-H valence oscillation, which is broad at the room temperature, splits up into two sharp components separated by only about 4 cm^{-1} from each other in the solid state at $-100°C$ The line 992 cm^{-1} shifts to 989 cm^{-1} when the liquid is solidified and cooled to $-180°C$. Similarly the frequency-shift of the line 607 cm^{-1} diminishes a little at the low temperature. On the other hand, the frequency shift of the line 849 cm^{-1} increases at low temperatures to 855 cm^{-1}.

The changes in position, number and intensity of the new lines in the low frequency region observed in the present investigation can hardly be explained by the theory put forward by Bhagavantam (1941) and Kastler and Rousset (1941). According to Bhagavantam the intramolecular vibration of the molecule as well as the angular oscillations of those molecules in the lattice may be of two types, symmetric and antisymmetric to the symmetry elements of the unit cell. The intensity of the Raman lines are assumed in this theory to be due to the change in the polarisability of the unit cell during the oscillation of the molecules in it. The benzene crystal belongs to an orthorhombic system in which the unit cell is pseudo-face-centred containing four molecules. The space group has been found by Cox (1932) to be V_h^{13}. If such a unit cell would execute a mode of oscillation in which the phases of all the four molecules were either the same or so adjusted as to make the oscillations antisymmetric to the symmetry elements of the unit cell, the frequencies of these two modes would be slightly different from each other. Thus each of the lines due to internal vibration of the benzene molecule would be split up into two components. No such splitting is actually observed, and on the contrary each of the lines becomes very sharp when this liquid is solidified. The line 3049 cm^{-1} is originally broad consisting probably of an unresolved doublet, and as each of the components becomes sharper in the solid state it is resolved from its companion. Thus this is not the splitting up of a single line into two components Hence the sharpness of the lines due to benzene in the solid state clearly shows that the scattering does not take place according to the theory put forward by Bhagavantam (1941) and that it is due to individual molecules. Also there are certain fallacies in the arguments in this theory mentioned above First, it is assumed that the unit cell acts as a large molecule and when one of the four benzene molecules executes any particular mode of internal oscillation, for instance, the breathing vibration, all the remaining three

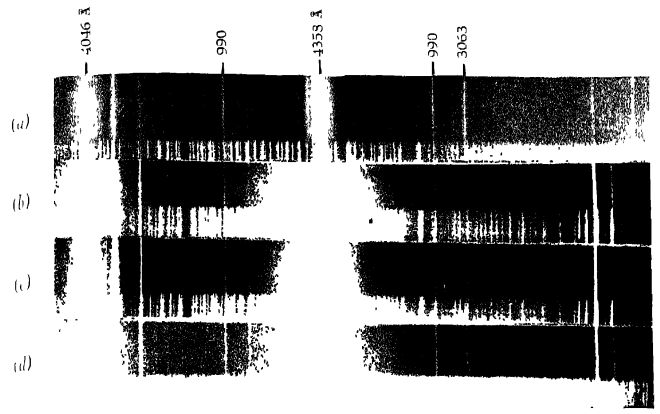

Fig 1

(*a*) Liquid at about 27 C
(*b*) Solid „ „ −10°C
(*c*) „ „ −100°C
(*d*) −180°C

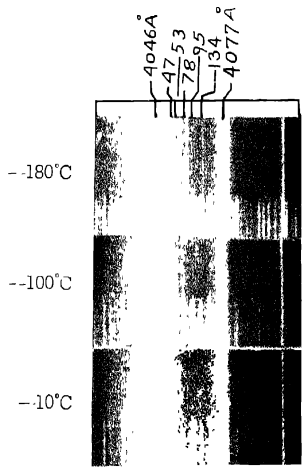

Fig. 2

Raman Spectra of benzene

molecules also execute the same mode of oscillation in only two distinct phases mentioned earlier. In fact, there is no reason to suppose that the remaining three molecules will execute the same mode of oscillation as the first one, and even if they do so, the relative phases may have any values. Hence the chance of having two distinct types of oscillation of the unit cell, in one of which the breathing vibrations of the molecules are all in phase and in the other the phases in the two molecules are opposite to those in the other two, is very small in comparison with that for the occurrence of this breathing vibration in any one of the four molecules independently. Thus the intensity of the scattering due to individual molecules is expected to be tremendously large in comparison with that due to the group of four molecules in this particular case. The extreme sharpness of all the prominent Raman lines of benzene in the solid state shows that the scattering is actually due to individual molecules. This question of probability of the occurrence of the definite phase relations in the oscillations of the different molecules in the unit cell has been overlooked by Bhagavantam (1941). Secondly, scattering takes place through a single election belonging to a particular molecule in the group of the four molecules in the unit cell in this particular case. If the change in the polarisability of the single molecule during any mode of vibration of the molecule determines the intensity of the corresponding line, the relative intensities of the Raman lines observed in the liquid are expected to remain unaltered in the solid state. If on the other hand, the change in the polarisability of the unit cell would determine the intensity of the corresponding Raman line during a mode of vibration of the four molecules in the unit cell, this change in polarisability would depend on the relative phases of the vibration of the four molecules and in that case the relative intensities of the prominent Raman lines would alter with the solidification of the substance. It can be seen from Plate VI that actually the relative intensities of the prominent Raman lines in the solid state are the same as those in the liquid state. Hence this fact also leads to the conclusion that in the crystal only scattering due to individual molecule is more predominant than that due to the group of four molecules in the unit cell. The change in the intermolecular field which takes place with the solidification of the substance may, however, alter slightly the frequencies of the Raman lines due to internal vibrations of the molecule. The changes in the frequencies of the lines which are observed to take place when benzene is solidified, as shown in Table I, are probably due to this increased effect of the intermolecular field in the solid state.

As regards the origin of new lines in the low frequency region Bhagavantam (1941) and Kastler and Rousset (1941) suggest that these are due to angular oscillations of the molecules pivoted in the lattice. In the present case, Rousset (1944) has assumed the line 35 cm^{-1} observed by Kastler and Fruhling (1944) at about 0°C to be due to complete rotation of the benzene molecule about an axis perpendicular to its plane,

because the line is totally polarised. It has already been pointed out that this line shifts to 53 cm^{-1} when the crystal is cooled down to $-180°C$. This fact shows that the line cannot be due to complete rotation of the molecule, because according to the theory of rotational spectrum of polyatomic molecules by Placzek and Teller (1933), the position of maximum in the rotation spectrum would shift towards the centre of the Rayleigh line with the lowering of temperature. The distance of the maximum from the centre of the Rayleigh line is proportional to $\sqrt{BkT}$, where $B=h^2/8\pi^2I$, I being the moment of inertia of the benzene molecule The value of I cannot diminish at low temperatures so rapidly as to keep the value of BT constant. Hence the frequency-shift of the line would be much smaller than 35 cm^{-1} at $-180°C$, had it been due to rotation of the molecule. Further, it is difficult to understand how a sharp line can be produced by complete rotation of the molecule, because several quantised states of rotation are possible. Hence the origin of the line is to be attributed to some other cause. As regards the origin of the other lines in the low frequency region Rousset (1944) has assumed that they are due to angular oscillations of the molecules about the two axes of the Crystal. If this assumption were correct, the amplitude and the frequency of the angular oscillation would diminish at low temperatures, because in the case of polar molecules in the liquid state it has been observed by previous workers including Sen (1950*a*) that the frequency corresponding to hindered rotation of the molecules diminishes at low temperatures and Sen (1950*b*) has observed that the amplitude becomes almost zero when the liquid is frozen. Since actually both the intensity and the frequency-shift of the lines increase with the lowering of temperature, the lines cannot be due to angular oscillation as postulated by the authors mentioned avove As pointed out by Sirkar and Gupta (1938) the new lines may be due to formation of virtual bonds between adjacent molecules.

The above arguments will indicate that the values of specific heat calculated on the assumption that the line 35 cm^{-1} is due to complete rotational freedom of the benzene molecule about an axis perpendicular to its plane have very little significance. Rousset (1944) has actually made such an assumption in calculating the specific heat of benzene and has further included the contribution from Einstein functions due to two lines at 55 cm^{-1} and 100 cm^{-1} respectively even at such low temperatures as 24°K and 36°K. It will be seen from Table I, however, that the frequency-shifts of the lines increase considerably even when the temperature is lowered only to about 93°K and they are expected to become still larger at 24°K. Further, two more lines appear at 47 cm^{-1} and 95 cm^{-1} respectively when the crystal is cooled to 93°K. These two lines have not been taken into consideration by Rousset (1944). These facts explain why he had to assume a very high value of the Debye temperature, e.g., 1150°K

for benzene which has a melting point of only 278°.5 K. On the other hand, Sirkar and Gupta (1938) assumed the Debye temperature of solid benzene to be as low as 121°.5 K and showed that if along with the Debye function Einstein functions due to the frequencies of the three lines 81 cm^{-1} 98 cm^{-1} and 124 cm^{-1} are taken into consideration, the calculated values of C_v agree closely with those observed throughout the range from 4°K to 70°K. It was also shown that at higher temperatures similar agreement is obtained if the internal oscillations of the molecules are taken into consideration.

Since the number of lines is larger than three, the calculations made by Sirkar and Gupta (1938) are to be revised now. Actually if these lines are taken as those due to oscillations of a pair of molecules in which virtual bonds have been formed each line will contribute only half of the Einstein function to the value of C_v. If the line 95 cm^{-1}, which is broad, is taken as a doublet, there are altogether six lines and only three frequencies are to be taken for calculating the contributions of the Einstein functions. The mean values of the frequencies of these three lines are expected to be about 58 cm^{-1} 90 cm^{-1} and 135 cm^{-1} respectively in the temperature range from 4°K to about 70°K. The corresponding values of θ_1, θ_2 and θ_3 in the function $E(\theta_n/T)$ are 83°.3, 129°.3 and 194° respectively. The values of $R\Sigma_1^3 E(\theta_n/T)$ and $3\,R.D\,(\theta'/T)$ with θ' equal to 121°.5 K are given in Table II. The values of C_p observed by Ahlberg, Blanchard and Landberg (1937) are given in the last column of the table. It will be observed that for temperatures 20°K, 30°K and 40°K the calculated values of C_v are slightly greater than those of C_p actually observed, but for the other temperatures the calculated values of C_v are slightly less than the observed values of C_p, as expected from theoretical point of view. Probably the frequency of the vibration corresponding to the line 53 cm^{-1} becomes a little larger than 58 cm^{-1} even at 40°K and if it is assumed that the frequency becomes about 64 cm^{-1} at 40°K the slight discrepancy observed at 20°K, 30°K and 40°K disappears. At temperatures lower than 10°K the contribution due to this line is so small in comparison with that due to the Debye function that the calculated values of C_v are not altered if the lowest frequency is increased to about 64 cm^{-1}. Similarly, at temperatures above 60°K the value of the frequency is probably slightly less than 58 cm^{-1}, because it diminishes to 53 cm^{-1} at 93°K.

Rousset (1944) has stated that the values of C_v of solid benzene calculated on the assumption that there is complete rotation of the molecule about an axis perpendicular to its plane even up to as low a temperature as 0.2°K agree with observed values. He has, however, overlooked the data published by Ahlberg, Blanchard and Landberg (1937) according to whom the values of C_p below 8°K are less than 0.14 cal/mol./degree. This fact completely disproves the hypothesis put forward by Rousset that the line

TABLE II

T	$3RD(\theta'/T)$	$R\sum_1^3 E(\theta_n/T)$	C_v Calc.	C_p (obs.)
4	017	00	.017	0195
8	132	007	.140	0.147
10	0 26	033	.29	0 346
20	1.54	.635	2.18	1 84
30	2 96	1.72	4 68	4.24
40	3 91	2 64	6.58	6.47
50	4 51	3 40	7 91	8.14
60	4 90	3 95	8.85	9 32
70	5 14	1 36	9 50	10 16

34 cm^{-1} observed by Kastler and Fruhling (1944) is due to complete rotation of the molecule. If on the other hand it is assumed that the rotation stops suddenly at a temperature between 15°K and 20°K the contribution of the Debye function with such a high value of θ_m as 1150° assumed by him would be too small to account for the observed values of C_p.

The facts mentioned above thus confirm the view expressed by Sirkar and Gupta (1938) that Einstein functions corresponding to the new Raman lines in the low frequency region observed in the solid state can explain satisfactorily the observed specific heats of benzene at low temperatures, and therefore, the facts lead to the conclusion that these lines are due to vibrations in a pair of molecules connected together by virtual bonds

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